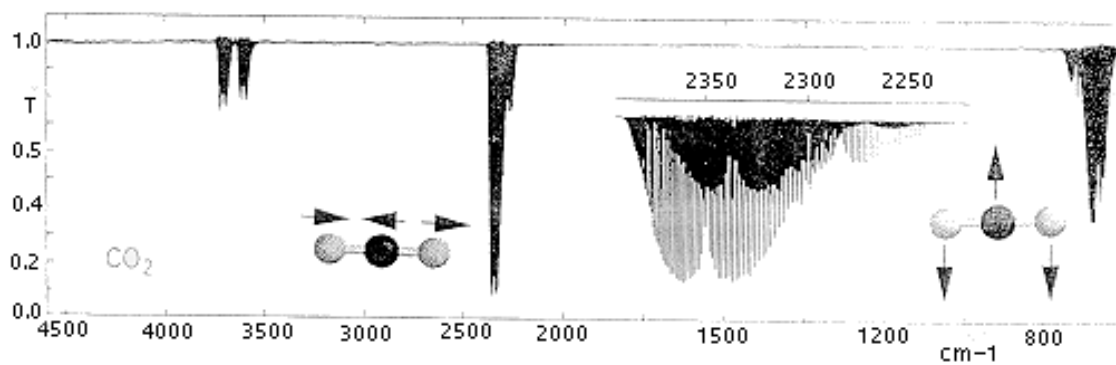


Physical chemistry
KEMS430

FTIR spectroscopy



3.4.2009

1 Theoretical background

To get theoretical background for understanding the FTIR spectrum of the CO₂ molecule, the following literature is recommended:

1. Hollas, J.M. *Modern Spectroscopy*, 4th Ed., 2004, John Wiley & Sons Ltd. Pages 41–63, 84, 103–113, 128–134, 137–179.
2. Atkins, P.W. and Friedman, R.S. *Molecular Quantum Mechanics* 3rd Ed. 1997, Oxford University Press. Pages 320–352.
3. Atkins, P.W. *Physical Chemistry* 8th Ed. 2006, Oxford University Press. Chapter 13 (Spectroscopy 1: rotational and vibrational spectra).

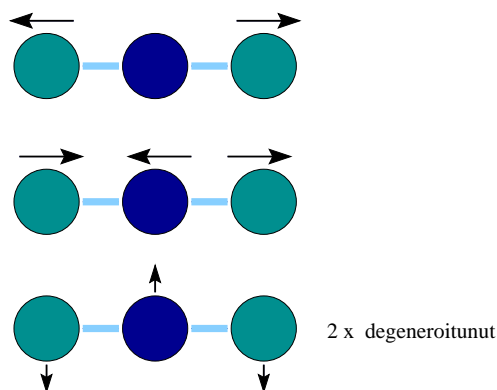


Figure 1: The four normal modes of a linear XY_2 molecule. The IR activity of Σ_u^+ and Π_u vibrations and the Raman activity of Σ_g^+ vibration can be deduced from the character table of the $D_{\infty h}$ point group.

Pay specific attention to the following aspects:

- Normal modes and determining them using character tables
- Vibrational and rotational energy level structure
- Formation of the vibrational spectrum and its rotational fine structure, including selection rules

- The effect of nuclear spin statistical weights on the rotational spectrum
- General features of FTIR spectroscopy (how it works, the advantages)

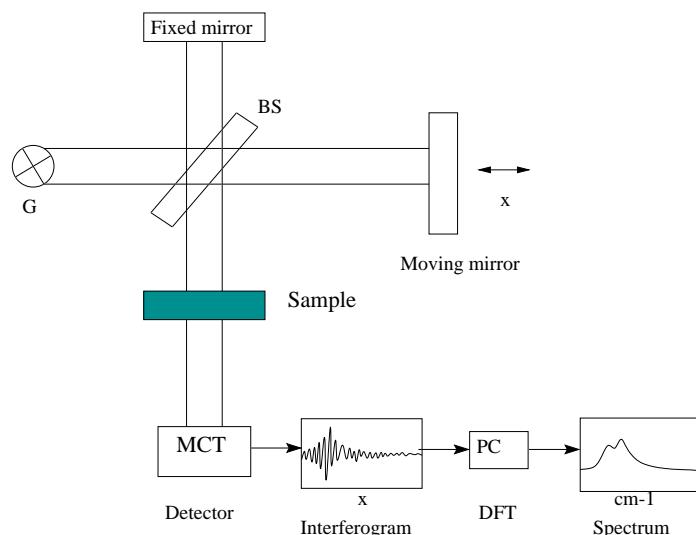


Figure 2: A FTIR spectrometer.

2 Measurement and analysis

Measure the FTIR spectrum for the carbon dioxide in the air with the FTIR spectrometer in the physical chemistry laboratory. Follow the instructions for the Cum Laude exercise 9, but extend the measurement range to 500 cm^{-1} (change the End [cm^{-1}] value to 500). Measure the spectra directly from the air without a sample cuvette. Hold the spectrometer sample hatch open for a while or blow into it before measurement to increase the amount of CO_2 in it. Note that as there is no sample cuvette, the spectrum is measured as a background only (Instrument \rightarrow Scan Background). Inspect the spectrum and note that the resolution of the spectrometer is not good enough for resolving the rotational fine structure.

The high resolution spectrum of carbon dioxide is found on the desktop, click on the “FTIR-spektri” icon. Print the spectrum (File \rightarrow Print).

Zoom into the 2500–2250 cm^{-1} spectral area to examine the rotational fine structure of this band more closely (outline the area by using the mouse and click inside it). To determine the peak positions, select Analyze \rightarrow Find Peaks. You can change the number of marked peaks by changing the position of the horizontal line and the Sensitivity. Print the zoomed spectrum, too. Then click the Replace-button and zoom only to the P-branch of the same band and print it. Compare this spectrum to the one measured with the lower resolution.

Interpret the spectrum:

- Recognize the bands from the water vapor in the air.
- Identify the normal modes of carbon dioxide and explain the possibly missing bands.

Calculate the structure and normal vibrations of carbon dioxide using the GAMESS program in the student laboratory computer using a 6-31G basis set (see Appendix A for the instructions). Compare the experimental spectrum with the spectrum calculated with the *ab initio* method.

Analyze the rotational fine structure:

- Notice and explain (using calculations) the convergence/divergence of the lines in the rotational fine structure (R and P branches)
- Find an explanation for the “forbidden” $\Delta J=0$ transition in the bending mode vibrational band (see for example ref.[1]).
- From the rotational fine structure, calculate the bond length of carbon dioxide and compare it to a literature value.

3 Literature

1. Hollas, J.M. *Modern Spectroscopy*, 4th Ed., 2004, John Wiley & Sons Ltd.
2. Hertzberg, G. *Molecular Spectra and molecular Structure, II. Infrared and Raman spectra of Polyatomic Molecules*, 1966, D. van Nostrand Company, Inc.
3. Schrader, B. *Infrared and Raman Spectroscopy, Methods and Applications*, 1995, VHC
4. Woodward, L.A. *Introduction to the Theory of Molecular and Vibrational Spectroscopy*, 1972, Clarendon Press, Oxford University Press
5. Atkins, P.W. *Physical Chemistry* 8th Ed. 2006, Oxford University Press
6. Atkins, P.W. and Friedman, R.S. *Molecular Quantum Mechanics* 3rd Ed. 1997, Oxford University Press

A Calculating the structure and vibrational frequencies using the GAMESS program

Before the Hartree-Fock calculations, the initial guess for the molecular structure has to be made. This is done using the Molden program, which is free for academic use just like GAMESS. The geometry is then optimized and the vibrational modes are calculated using GAMESS, and the results are again viewed with Molden.

Drawing a molecule using Molden

The first objective is to draw the molecule and save the initial guess of structure for the use in the Hartree-Fock calculation.

1. Open the “Molden” program by clicking “X” in the bottom task bar, typing “molden” in the opened window, and pressing Enter.
2. Click on the “ZMAT Editor” button.
3. Add the first atom by clicking “Add Line” and by selecting the right element from the periodic table.
4. Add the second atom by clicking “Add Line”, selecting again the right element from the table, and clicking the first atom appeared as a ball in the “Molden” window. (Note: the first click activates the window and the second click selects the atom.)
5. If you make a mistake, you can remove the last added atom by clicking “Delete line”.
6. Add the last atom as before, but now click the both ends of the lines representing the two earlier atoms.
7. Now there should be three lines in the “Zmatrix Editor” window, describing the structure (elements, bond lengths and angles) of the molecule.

8. Save the Z-matrix by writing a file name (for example “MyCO2.zmt”, without the quotes, but with the file extension .zmt) in “File name ?” and click “Write Z-Matrix”.
9. Quit Molden by clicking “Close” and then the skull symbol.
10. Do not close the “xterm” window. If you did it anyway, you will find the window again by clicking “X” in the bottom task bar and then selecting “Applications” and “Terminal” from the toolbar at the top.

Geometry optimization

After drawing the molecule, the geometry can now be optimized. In the geometry optimization, the wavefunction of the molecule is solved using the Hartree-Fock method, and the forces acting on different nuclei are calculated, after which the nuclei are moved according to the forces. This process is repeated until a conformation, where no forces are present, is found, meaning that the equilibrium geometry of the molecule is solved. Here, a 6-31G basis set is used, meaning that each inner atomic orbital is constructed using a linear combination of six Gaussian functions, and the valence orbitals are constructed of four Gaussians, of which one is stretched further away in space from the nucleus to aid the accommodation of the orbital to its environment. In the execution of the calculation, the JGaussJob program is used to build the commands for the GAMESS program, using the Z-matrix you just made. The commands are then used to do the geometry optimization using the Hartree-Fock method.

1. Open the “JGaussJob” program. Select your Z-matrix file (MyCO2.zmt) by clicking “Browse Jobs”. The file should be in the “MMCumu” folder, select it by clicking its name. (Now your file name should appear after the “Job file:” text.)
2. Choose the geometry optimization process using the 6-31G basis by selecting “Do Geometry optimization using 6-31G basis.”

3. Start the job by clicking “Execute job”. Wait until the “Wait...” text changes back to “Execute job”, indicating that the optimization process is finished.
4. Quit the program (the red ball button at the top of the window).

The optimized structure of the molecule

The optimized structure of the molecule can now be viewed using the Molden program.

1. Open the “Molden” program again.
2. Open the log file of the calculation by clicking “Read”, selecting the log file of your calculation (“MyCO2.log”) and clicking “Close”.
3. The log file consists of several Z-matrices. Select the last, optimized, one by clicking “Movie”.
4. Measure the bond length by clicking first “Distance” and then click the two atoms between which the bond is (for example C and O). Remember to write down the value! (Note again that the first click on the window only activates it, and the following ones select the atoms.)
5. Measure the bond angle by clicking “Angle” and by clicking the three atoms forming the angle. Write down the value.
6. Compare the computational results to the literature values.
7. If you wish, you can also view the molecular orbitals by clicking “Dens. Mode”, selecting the “Space” mode by clicking the button, giving a “Contour value” 0.1 and by pressing “Enter”. Then press “Fill”.
8. The orbitals can now be viewed by clicking “Orbital” and by selecting the orbitals from the list. The molecule can be rotated in the window by pressing the mouse button down.

9. Quit the program by clicking the skull symbol.

Calculation of the vibrational modes and frequencies

The vibrational modes can be calculated after the geometry optimization. The bonds are described as harmonic oscillators, and their force constants are calculated based on the electronic wavefunction. The vibrations are coupled, if the force constants are of the same magnitude. These vibrations are called the normal modes and their frequencies are the vibrational frequencies of the molecule.

1. Open the “JGaussJob” program. Select the optimized Z-matrix, that has a definition “_opt” between the name and the file extension (“MyCO2_opt.zmt”).
2. Choose the vibrational analysis using the same basis as before by selecting “Do Vibrational analysis using 6-31G basis.” (Note: The basis set has to be the same that was used in the geometry optimization.)
3. Start the job by clicking “Execute job”. Wait until the “Wait...” text changes back to “Execute job”, indicating that the calculation is finished.
4. Close the program.

Viewing the vibrational modes

The vibrations can now be viewed with the Molden program.

1. Open the “Molden” program.
2. Open the log file of the calculation by clicking “Read”, selecting your file (“MyCO2_opt.log”), and clicking “Close”.

3. Select a ball-and-stick model for viewing by clicking “Solid”, selecting “Ball & Stick”, and clicking “Shade”
4. The vibrational modes can be selected by clicking “Norm. Mode”, which will also show the spectrum. Close the spectrum. (If “Norm. Mode” is not visible, you probably forgot to use the “Vibrational analysis” command.)
5. Select the frequency you want to view from the list in the “Molden Frequency Select” window. You can also see the rotations and translations at the lower frequencies. In the true vibrations, the molecule changes its shape. You can rotate the molecule by pressing the mouse button down, to see the vibrations better. Write down the vibrational frequencies and the corresponding modes (symmetric/antisymmetric stretch, bend, etc.), and compare the results with the experimental spectrum.
6. Quit the program by clicking the skull symbol.